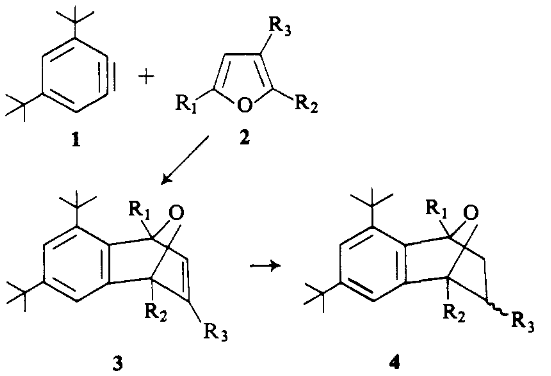
1,8-Di-*t*-butylnaphthalenes

Sir:

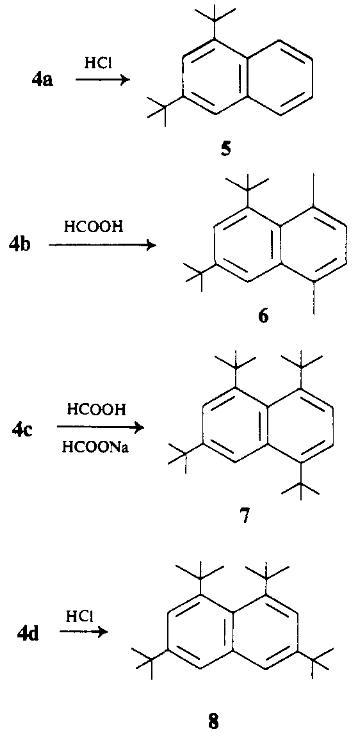
The strain energy in *o*-di-*t*-butylbenzene, 22 kcal/mol,[1] is detected in bond angle distortion,[2] facile extrusion of a *t*-butyl group,[1,3] and small perturbation of aromaticity.[1]

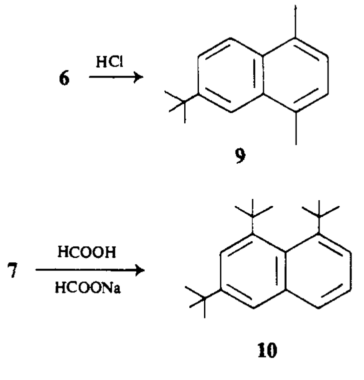
A priori, the 1,8-di-*t*-butylnaphthalene system seems to be more crowded than the benzene analog. We wish to report direct syntheses of the naphthalene system. Our approach involves Diels–Alder reaction of the benzyne **1** (generated from 3,5-di-*t*-butylanthranilic acid) with the appropriate furan **2** to form the endoxide **3**.[4] The yields of **3a** and **3b** were high (90%), whereas **3c** was formed in 10% yield, presumably because the transition state for the last case is extremely crowded. The Diels–Alder reaction is so unfavorable that the major product is 1,3,5,7-tetra-*t*-butylacridone, a condensation product of benzyne with anthranilic acid.[5] Thus the reaction of benzyne **1** with furan **2d** was predicted to result in the 1,3,5,7 substitution pattern with only *t*-butyl *vs.* hydrogen interactions in the transition state. The actual obtention of the 1,3,6,8 product **3d** (>50% yield) is suggestive of a transition state where bond formation between the two unhindered positions of the benzyne and the furan is taking place before the second bond of the cycloadduct is formed. The endoxides **3** were converted to the dihydroendoxides **4** *via* catalytic hydrogenation. Dehydration of **4a** and **4d** was catalyzed with ethanolic HCl to afford naphthalenes **5** and **8**.[6] Formic acid served as the catalyst for the aromatization of **4b** to naphthalene **6**, a fused ring analog of *o*-di-*t*-butylbenzene.[7] Buffered formic acid was used to dehydrate **4c** to yield **7**.



a, $R_1 = R_2 = R_3 = H$
b, $R_1 = R_2 = CH_3$; $R_3 = H$
c, $R_1 = R_2 = t\text{-Bu}$; $R_3 = H$
d, $R_1 = R_3 = t\text{-Bu}$; $R_2 = H$

Whereas naphthalene **5** was stable to HCl, the crowded system **6** readily extruded the *peri*-*t*-butyl group when treated with HCl to form **9**. This behavior corresponds to that of the benzene series with the only variance being the mildness of the conditions in our case.[1,3] With the *peri*-di-*t*-butyl system **7**, formic acid suffices to protonate the ring and catalyze de-*t*-butylation with the loss of the less strained α-t-butyl,[8] leaving intact the tri-*t*-butylnaphthalene **10**. The *peri* crowded structure **10** is readily derived from nmr data in Table I, that is, the disappearance of the α-*t*-butyl and a deshielded *peri* H. The inertness of the most strained position is again seen in the relative stability of naphthalene **8** to HCl. Thus, the *peri*-di-*t*-butylnaphthalene system appears to be a new class of crowded molecule, where strain energy raises the ground state of an aromatic system to a level where formic acid serves to protonate the ring, but where the crowding is so great that protonation at a site that would permit relief of strain is not allowed.





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(1) E. M. Arnett, J. C. Sanda, J. M. Bollinger, and M. Barber, *J. Am. Chem. Soc.*, **89**, 5389 (1967).

(2) A. van Bruijnsvoort, L. Eilermann, H. van der Meer, and C. H. Stam, *Tetrahedron Lett.*, 2527 (1968).

(3) A. W. Burgstahler, P. Chien, and M. O. Abdel-Rahman, *J. Am. Chem. Soc.*, **86**, 528 (1964).

(4) (a) 2,5-Di-*t*-butylfuran: A. Ramasseul and A. Rassat, *Bull. Soc. Chim, France*, 2214 (1963); (b) 2,4-di-*t*-butylfuran: E. E. van Tamelen and T. H. Whitesides, *J. Am. Chem. Soc.*, **90**, 3895 (1968).

(5) (a) S. F. Dyke, A. R. Marshall, and J. P. Watson, *Tetrahedron*, **22**, 2515 (1966); (b) R. Howe, *J. Chem. Soc.*, *C*, 478 (1966).

(6) Naphthalene **5** may have been formed in a mixture of products obtained by reaction of *t*-butyllithium with naphthalene: J. A. Dixon and D. H. Fishman, *J. Am. Chem. Soc.*, **85**, 1356 (1963).

(7) M. A. Frisch, C. Barker, J. L. Margrave, and M. S. Newman, *ibid.*, **85**, 2356 (1963).

(8) The α-*t*-butyl group in naphthalenes is somewhat strained and subject to expulsion since Friedel–Crafts *t*-butylation of naphthalene affords only β substitution: A. Schreisheim, "Friedel–Crafts and Related Reactions," Vol. II, Part I, G. Olah, Ed., Interscience Publishers, New York, N. Y., 1961, Chapter XVIII.

Table I. Nmr Data for *t*-Butylnaphthalenes[a]

Compd	*t*-Butyls			Other resonances
	β	α	*peri*	
5[b]	1.40	1.64		7.17–7.28 (3, m), 8.30 (1, m, *peri* H)
6	1.42	1.59		2.61 (3, s), 2.77 (3, s, *peri* CH_3), 6.99 (2, s), 7.66 (1, d, J = 2 Hz), 7.72 (1, d, J = 2 Hz)
7	1.42	1.57	1.22 1.24	7.10 (1, d, J = 8 Hz), 7.28 (1, d, J = 8 Hz), 7.43 (1, d, J = 1.8 Hz), 7.90 (1, d, J = 1.8 Hz, *peri* H)
8	1.40		1.30	7.22 (2, d, J = 1.7 Hz), 7.48 (2, d, J = 1.7 Hz)
9	1.40			2.58 (3, s), 2.62 (3, s), 7.03 (2, s), 7.46 (1, dd, J_{bc} = 9, J_{ac} = 2 Hz), 7.83 (1, d, J_{bc} = 9 Hz), 7.83 (1, d, J_{ac} = 2 Hz)
10	1.40		1.27 1.28	7.1–7.6 (5, m)

[a] In parts per million. [b] The assignments for *t*-butyl and *peri* H are consistent with data for 1,4-di-*t*-butylnaphthalene: R. W. Franck and K. Yanagi, *J. Org. Chem.*, **33**, 811 (1968).

An observation about the nmr data for the *peri* di-*t*-butyl groups can be made: the signals appear as sharp singlets, upfield from the "normal" naphthalene *t*-butyl resonances. This may be rationalized by postulating that the *peri* groups relieve crowding by bending away from each other above and below the plane of the naphthalene ring. Thus locking and/or restricted rotation of the *t*-butyl groups (and line broadening) is avoided and the protons are not in the zone of maximum deshielding. Also, this spatial arrangement of the *t*-butyl groups, as seen from models, serves to hinder the *peri* ring carbons from external acid attack.

A comparison of uv spectra (Figure 1) of the 1,3,5,8 systems **6** and **7** with 1,3,5,8-tetramethylnaphthalene is indicative of the very great strain in **7**. Similar uv spectral perturbations are observed for **8** and **10**. The spectrum of the *o*-di-*t*-butylbenzene analog **6** shows the expected slight bathochromic shifts, slight decreases in extinction, and the loss of fine structure compared to the model compound. The large deviations in the spectrum of the tetra-*t*-butyl compound **7** are good physical evidence for significant perturbation of the aromatic system.[9] When the requisite model compounds can be obtained, it is our plan to apply other physical measurements discussed by Arnett[1] to determine semiquantitatively the strain energy of our system. Also, X-ray crystallographic structural analyses and further chemical investigations are under way.[10,11]

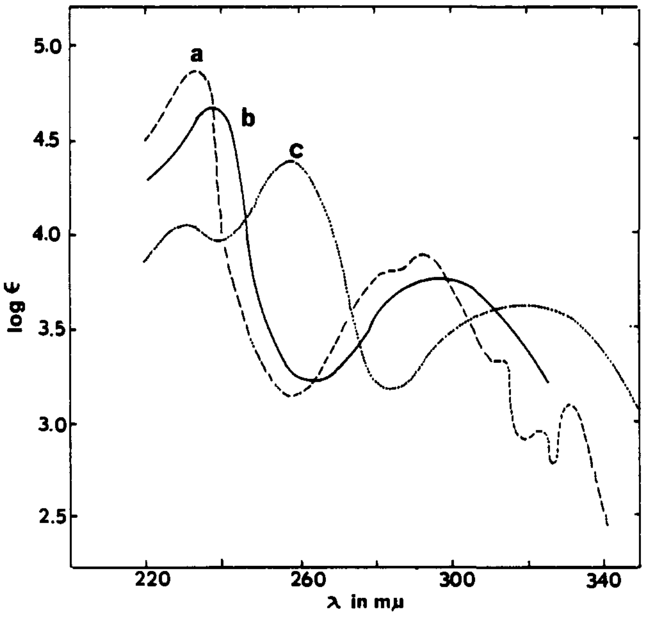

Figure 1. Uv spectra of 1,3,5,8-tetraalkylnaphthalenes: (a) 1,3,5,-8-tetramethylnaphthalene (W. L. Mosby, *J. Am. Chem. Soc.*, **75**, 3348 (1953)); (b) 1,3-di-*t*-butyl-5,8-dimethylnaphthalene (**6**); (c) 1,3,5,8-tetra-*t*-butylnaphthalene (**7**).

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(9) J. Dale, *Chem. Ber.*, **94**, 2821 (1961).

(10) Correct elemental analyses were obtained for all compounds reported.

(11) (a) Portions of this work were previously reported: R. W. Franck and E. Leser, Abstracts, 156th National Meeting of the American Chemical Society, Atlantic City, N. J., Sept 1968, ORGN-167. (b) Financial assistance was received from the New York State Science and Technology Foundation for the purchase of a Varian A-60A spectrometer, from the National Science Foundation for a traineeship for E. L. and for partial research support through Grant GP 7754, and from Fordham University research funds.

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Migratory Aptitudes in a Thermal, Sigmatropic Rearrangement

Sir:

Sigmatropic reactions[1] of neutral molecules are of special interest because they are controlled by the conservation of orbital symmetry.[2] These reactions involve intramolecular migration of a group from one carbon to another, and an obvious experiment is to compare the migratory aptitudes of various groups in these reactions with those found in other rearrangements. The purposes of such a comparison are to provide predictive power over

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(1) G. B. Gill, *Quart. Rev.* (London), **22**, 338 (1968).

(2) R. B. Woodward and R. Hoffmann, *J. Am. Chem. Soc.*, **87**, 2511 (1965).